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LETTER

Synthesis, electrochemical and spectroscopic properties of pendant hydroquinone- and quinone-substituted polypyridyl ruthenium(II) complexes

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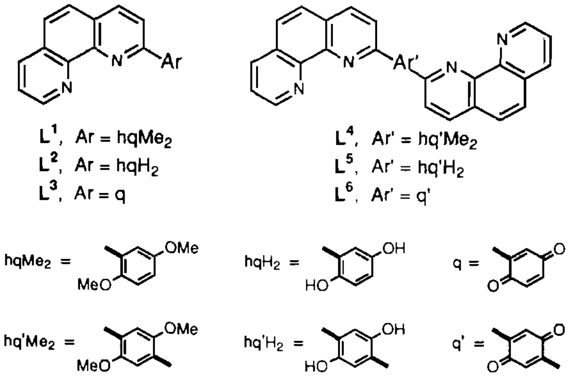
We have targetted parahydroquinonyl-substituted and parabenzoquinonyl-substituted ligands, such as phenanthrolinyl ligands L^1–L^6, principally in order to investigate complexes with coordinated hydroquinonyl or quinonyl groups (e.g. O,N,N-coordination for L^1–L^3 and bridging $(O,N,N)_2$-coordination for L^4–L^6 [1]. Complexes in which the hydroquinonyl or quinonyl moiety can only act as a pendant group have also been prepared. This letter describes the preparation, spectroscopic and redox properties, and some preliminary luminescence measurements of N,N-coordinated complexes of L^1–L^5 with the $Ru(bpy)_2{}^{2+}$ fragment. Analogous, tris-diimmine ruthenium(II) complexes have been and continue to be the centre of much attention because they are highly luminescent species capable of sensitizing a wide variety of photoredox reactions [2]. The electron transfer reactions of quinones and hydroquinones play a pivotal role in photosynthesis, for example quinones are the primary electron acceptors in photosystem I [3]. The obvious implication is that quinonyl-substituted tris-diimmine ruthenium(II) complexes may have a role in artificial photosynthetic systems [4]. To the best of our knowledge there are, rather surprisingly, no prior literature reports of tris-diimmine ruthenium(II) complexes substituted by pendant quinones [5]. This communication is also the first report of quinonyl-substituted L^3 and bridging ligands L^4, L^5.



The syntheses of L^1 and L^4, protected precursors of the hydroquinonyl- and quinonyl-substituted ligands, are based on the facile direct addition of aryllithium reagents to aromatic polyimmine compounds [6]. Reaction of monolithiated 1,4-dimethoxybenzene [7] with one equivalent of 1,10-phenanthroline followed by rearomatization with excess MnO_2 gave pale yellow L^1 (m.p. 162 °C, 93%). Bridging ligand L^4 was isolated from the analogous reaction of dilithiated 1,4-dimethoxybenzene [7] with two equivalents of phenanthroline as a yellow powder (m.p. 269 °C, 32%) along with L^1 (51%).** The yellow hydroquinonyl-substituted ligands L^2 (m.p. 240 °C) and L^5 (m.p. > 360 °C) were obtained by deprotection of L^1 and L^4, respectively, either with pyridinium hydrochloride heated at reflux [8] or with BBr_3 in dichloromethane [9]. Yields by both routes were above 80%. To date, attempts to obtain uncomplexed quinonyl-substituted ligands L^3 and L^6 have failed. For example, neither oxidative cleavage of the dimethoxyphenyl-substituted ligand L^1 (or L^4) with Ce^{4+} in acetonitrile–water mixtures [10] nor direct oxidation of the pendant hydroquinone L^2 (or L^5) with 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ) [11] gave the targetted ligand, L^3 (or L^6).

Reactions of either L^1 or L^2 with one equivalent of $[Ru(bpy)_2Cl_2]$ in 2-methoxyethanol heated at reflux gave the bis(2,2'-bipyridyl)ruthenium(II) complex cations $[Ru(bpy)_2(L^1)]^{2+}$ (1) (68%) and $[Ru(bpy)_2(L^2)]^{2+}$ (2) (75%; ν(O–H): 3640 cm^{-1}), respectively. The dimethoxyphenyl-bridged dimer $[\{Ru(bpy)_2\}_2(L^4)]^{4+}$ (4) (88%) and the hydroquinonyl-bridged dimer $[\{Ru(bpy)_2\}_2(L^5)]^{4+}$ (5) (77%; ν(O–H): 3650 cm^{-1}) were obtained from analogous reactions of L^4 and L^5 with two equivalents of $[Ru(bpy)_2Cl_2]$. Reaction of L^4 with only one equivalent of $[Ru(bpy)_2Cl_2]$ gave

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**Separation of L^4 from L^1: excess $[Cu(MeCN)_4]BF_4$ was added to the crude mixture of L^1 and L^4 in ethanol, the precipitated mixture of $[Cu(L^1)_2]BF_4$ (soluble) and $[Cu(L^4)_2]_n(BF_4)_n$ (insoluble polymer) was separated by exhaustive Soxhlet extraction with acetone, and the free ligands were obtained by treatment of the Cu(I) complexes with excess potassium cyanide in water–methanol solution.

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$[Ru(bpy)_2(L^4)]^{2+}$ (**7**) (70%), which has a pendant phenanthrolinyl group that can be used in the construction of oligomeric complexes with terminating $Ru(bpy)_2(L^4)$ moieties (e.g. the tetrameric complexes $[\{(bpy)_2Ru(L^4)\}_3M]^{8+}$ (M = Ru and Os)) [12]. Direct oxidation of the hydroquinonyl-substituted **2** with DDQ in dichloromethane gave the pendant quinonyl-substituted $[Ru(bpy)_2(L^3)]^{2+}$ (**3**) (65%; ν(C=O): 1662 cm^{-1}). However, DDQ does not oxidize the pendant bridging-hydroquinonyl group in dimer **5** and yield the quinonyl-bridged dimer $[\{Ru(bpy)_2\}_2(L^6)]^{4+}$ (**6**). Similarly, attempted direct oxidative deprotection of **4** with Ce^{4+} in water–acetonitrile failed to yield **6**. Molecular modelling studies show that the bridging dimethoxyphenyl group in **4** and the bridging hydroquinonyl group in **5** lie almost entirely enclosed in a pocket formed by the two linked $Ru(bpy)_2{}^{2+}$ moieties. Presumably, the attempted synthesis of **6** failed because the bridging aryl groups in **4** and **5** are inaccessible and unreactive.

All complexes were purified as their chloride salts by repeated size exclusion chromatography (Sephadex LH-20 support and methanol eluent), and were then precipitated from saturated aqueous NH_4PF_6 solutions as their $PF_6{}^-$ salts (overall yields are quoted above). Elemental analyses for **1**–**5** and **7** are consistent with their formulations. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **1**–**3** are complicated and have not been fully assigned. The complexity arises from the fact that *all* bipyridyl and phenanthrolinyl atoms are inequivalent. The ^1H NMR peaks from the pendant substituents in **1**–**3** are, however, well separated from the bipyridyl and phenanthrolinyl resonances. In the respective ^1H NMR spectrum of **1**–**3**, two sets of multiplets with approximately equal integrated intensity were observed for each magnetically non-equivalent pendant proton. This suggests that steric crowding prevents rotation of the pendant substituent thus leading to a pair of atropisomers (restricted rotational isomers) [13] for each complex. This is illustrated in Fig. 1 which shows the quinonyl region from a ^1H–^1H correlation spectrum of **3**. Two sets of quinonyl multiplets arising from **3a** and **3b** are identifiable. Four carbonyl peaks at δ 187.11, 186.84, 186,68 and 185.95 were observed in the $^{13}C\{^1H\}$ NMR spectrum of **3**. Dimers **4** and **5** were isolated as mixtures of *meso* and chiral diastereomers further complicating their NMR spectra [14]. For example, four methoxy peaks (one peak for the two equivalent methoxy groups of each atropisomer of the *meso* diastereomer, and two peaks for the two inequivalent methoxy groups in each of the two atropisomers of the chiral diastereomers) are expected in the ^1H NMR spectrum of **4**, and are observed.

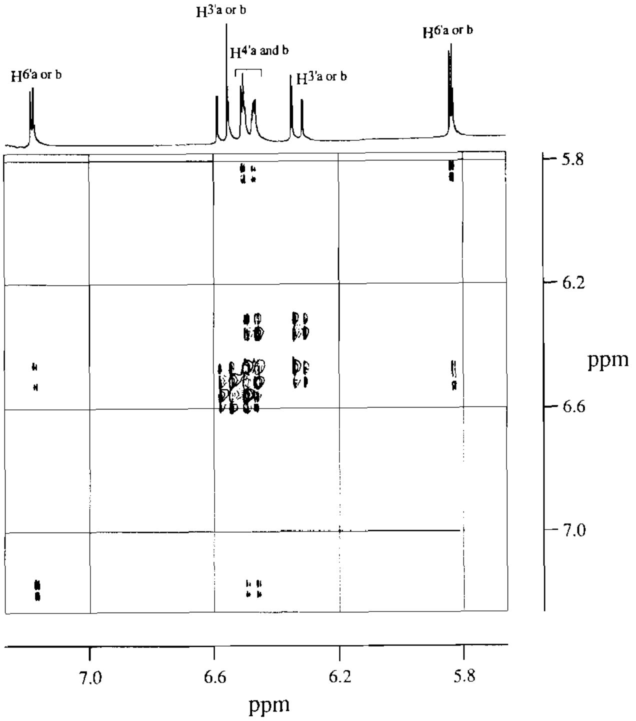
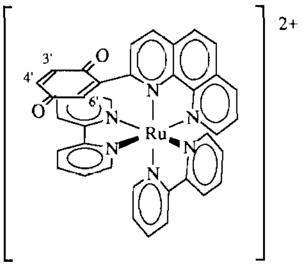
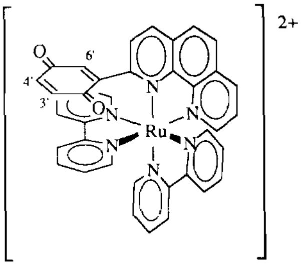


Fig. 1. The quinonyl region of a ^1H–^1H COSY NMR spectrum of **3** at 300 MHz in $(CD_3)_2CO$ at 25 °C.



3a



3b

The electrochemistries of **1**–**5** and **7** have been characterized by cyclic voltammetry and differential pulse polarography in acetonitrile solutions containing n-Bu_4NPF_6 as supporting electrolyte. Data are collected in Table 1. Each complex showed a reversible Ru(III)/Ru(II) couple [15] at approximately 0.9 V versus Fc^+/Fc with a 60 mV peak-to-peak separation (ΔE_p). The ΔE_p values are consistent with a one-electron electrochemical process and indicate that the metal centres in dimers **4** and **5** are non-interacting [16]. The current of the Ru(III)/Ru(II) couple relative to the current of the pendant redox processes was doubled in dimers **4** and **5**. The electrochemical responses observed for the pendant moieties were as expected (e.g. Fig. 2). (i) Quasi-reversible one-electron oxidation ($i^c/i^a \sim 1.0$ but $\Delta E_p \gg 60$ mV) of the dimethoxyphenyl pendant [17] is observed in the voltammograms of **1**, **4** and **7**. (ii) In **2** and **4** irreversible two-electron (by comparison with

TABLE 1. UV–Vis absorption, emission, lifetime and electrochemical data for complexes **1**–**5** and **7**

Complex	Absorption (300 K)	Emission (77 K)		$E_{\mathrm{RuIII/RuII}}$[e] (mV)	E_{pendant}[e] (mV)	E_{ligand}[e] (mV)
	λ_{max} (nm) (ϵ (10^4 M^{-1} cm^{-1}))[a]	λ_{max}[b] (nm)	τ[c] (μs)			
1	269 (4.5), 287 (5.5), 422 (sh), 448 (1.1)	587, 630, 675 (sh)	4.95 ± 0.05	890[f]	1230[g]	−1730[f]
2	269 (5.0), 287 (5.8), 422 (sh), 447 (1.3)	583, 626, 673 (sh)	5.40 ± 0.05	930[f]	760[h], −300	−1780[g]
3	268 (6.1), 287 (5.8), 420 (sh), 441 (1.4)	588, 629, 670 (sh)	2.2[d]	936[f]	−690[f]	−1780[h]
4	269 (sh), 287 (12.8), 423 (sh), 448 (1.6)	587, 634, 678 (sh)		910[f]	1910[g]	−1710[h]
5	269 (sh), 287 (13.4), 423 (sh), 449 (2.6)	591, 635, 680 (sh)		1020[f]	840[h], −280	−1740[g]
7	269 (6.9), 287 (7.7), 422 (sh), 449 (1.3)	594, 636, 685 (sh)		810[f]	1350[g]	−1730[g]

[a] Measured in CH_3CN. [b] From uncorrected emission spectra at 77 K in Nafion 117 (350.7/356.4 nm (Kr^+ laser) excitation). [c] Lifetimes at 77 K in Nafion 117, measured using 3 ns N_2 laser excitation and detected at 618 nm. [d] Not a single exponential decay. [e] From cyclic voltammetric measurements in CH_3CN (0.1 M n-Bu_4NPF_6). Potentials are given vs. the Fc^+/Fc couple. [f] Reversible. [g] Quasi-reversible. [h] Irreversible.

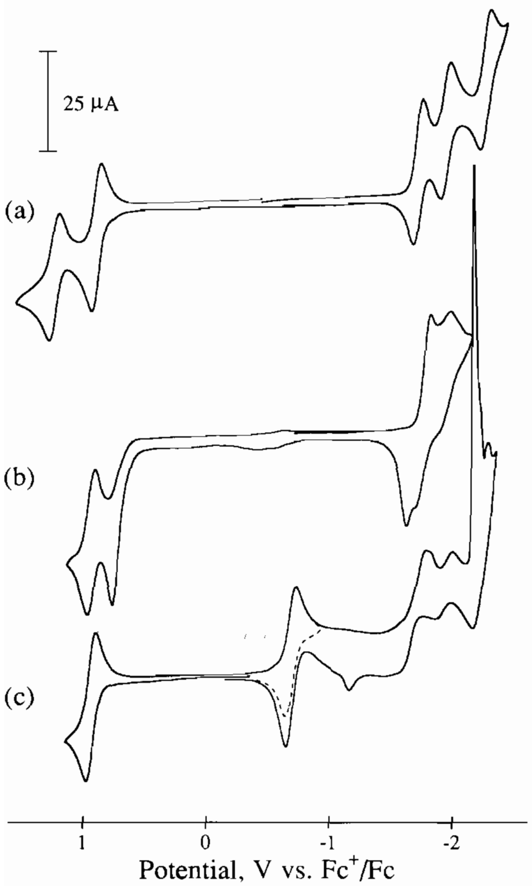


Fig. 2. Cyclic voltammograms of *c*. 1×10^{-3} M solutions of (a) dimethoxyphenyl-substituted **1**, (b) hydroquinonyl-substituted **2** and (c) quinonyl-substituted **3** in acetonitrile (0.1 M n-Bu_4NPF_6) at Pt disk electrode. Scan rate: 100 mV s^{-1}.

the peak currents for the Ru(III)/Ru(II) couple) oxidation of the hydroquinonyl pendants ($hqH_2 \rightarrow q/H^+ + H^+ + 2e$) occurs prior to the Ru(III)/Ru(II) couple and gives rise to a coupled peak ($q/H^+ + H^+ + 2e \rightarrow hqH_2$) in the reverse cathodic scan at approximately −0.3 V [18]. (iii) Quinonyl-substituted **3** exhibited a reversible one-electron reduction to the semiquinone (i.e. for the quinone–semiquinone couple) at −0.69 V [19]. Values for the first diimine-ligand-centred reduction [12] of **2**–**5** and **7** are given in Table 1. These reduction processes were complicated by adsorption and stripping phenomena (e.g. Fig. 2). Only **1** showed three reversible one-electron ($\Delta E_p = 60$ mV) diimine-ligand-centred reductions (at −1.73, −1.95 and −2.28 V, Fig. 2(a)).

The electronic spectra of **1**–**5** are characterized by several intense bands in the UV and visible regions (Table 1). Comparison with the spectra of the free ligands and the spectra of $[Ru(bpy)_{3-n}(phen)_n]^{2+}$ ($n = 1$–3) derivatives [20] allows assignment of the bands at about 270 and 290 nm to ligand-centred (LC) phenanthrolinyl and bipyridyl π–π^* transitions, respectively, and the visible bands to $d\pi(Ru)$–π^*(ligand) metal-to-ligand charge-transfer (MLCT) transitions. Notably, the MLCT band of quinonyl-substituted **3** is blue-shifted by 6 nm compared to **1** and **2**.

Preliminary luminescence measurements [21] have been obtained for **1**–**5** in Nafion 117 membranes [22]** at 77 K. Complexes were exchanged at low levels into the protonated Nafion membranes. **1**–**5** are luminescent in this matrix at 77 K (Table 1) and the emission spectra of the complexes show characteristic progressions spaced by 1150–1270 cm^{-1}. The band profiles and energies of the luminescence spectra are all very similar to those found for other $[Ru(bpy)_{3-n}(phen)_n]^{2+}$ ($n = 1$–3) complexes [20], thus allowing assignment of the emitting state to a ^{3}MLCT level. The steady-state emission of quinonyl-substituted **3** is substantially weaker than that of dimethoxyphenyl-substituted **1** or

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**The samples for luminescent measurements were prepared as follows: a 1.0 cm^2 square of protonated Nafion 117 membrane was suspended in a slowly stirred dilute solution of the appropriate complex in neutral aqueous acetonitrile for 2 h; the Nafion membrane was then removed from the solution, rinsed several times with distilled ethanol and then air dried.

hydroquinonyl-substituted **2**. This suggests that the luminescence of **3** is quenched by the quinonyl pendant and is consistent with previous studies which have shown rapid luminescence quenching of excited $[^*Ru(bpy)_3]^{2+}$ by added quinones [23]. Lifetime measurements on monomeric complexes **1–3** confirm this with a reduction in the 77 K lifetime from 5.0 μs for **1** and 5.4 μs for **2** to 2.2 μs for **3**. Luminescence decay curves for **1** and **2** are single exponential at 77 K as are the decay curves of analogous mixed-ligand ruthenium(II) complexes [20]. However, the decay curve of quinonyl-substituted **3** cannot be fitted to a single exponential. Possible contributory factors are (i) the complex can occupy different domains within the Nafion membrane [22] and, in particular, the pH variation within the domains is expected to influence the rate of quinone quenching [24], and (ii) it has been demonstrated that **3** exists as atropisomers **3a** and **3b** — these may behave differently. More detailed studies of the photophysical properties of **1–5** and analogous complexes are planned and will be included in a full report of this work.

Supplementary material

Listings of spectroscopic data for L^1, L^2, L^4, L^5 and complexes **1–5** and **7**, and figures of the cyclic voltammograms, UV–Vis and emission spectra for all complexes are available on request from author S.B.C.

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